Simulating Solvent Effects and Liquid Behavior with the Effective Fragment Potential Method

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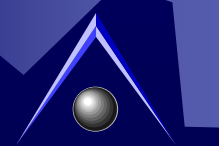


AMES LABORATORY

Outline

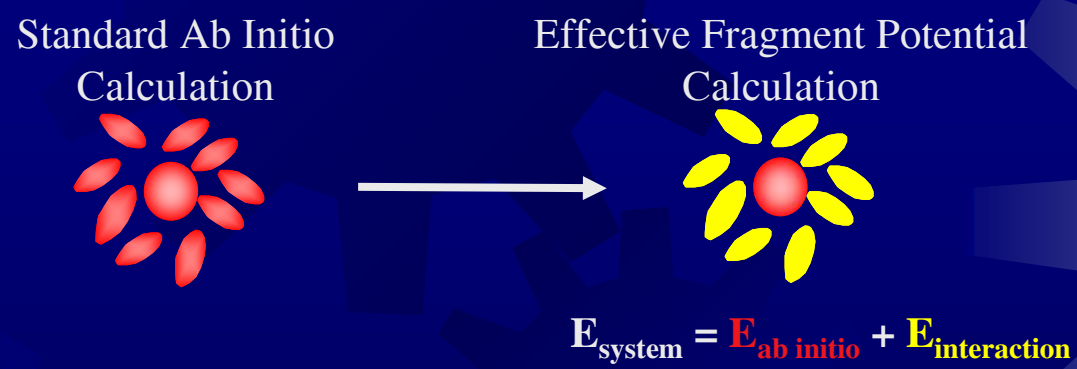
- Effective Fragment Potential method overview (EFP1)
- Further developments:
  - EFP1/DFT
  - EFP1/MP2
  - EFP2
- Using EFP:
  - Molecular Dynamics
  - Parallel EFP code

Why should YOU care??

- Understanding the environment
  - Most processes occur in the condensed phase
  - Biological applications
- Solvation models in use:
  - Continuum
  - Discrete
- Model to reliably predict BOTH cluster AND bulk properties

Effective Fragment Potential Method (EFP)

- Effective Fragment Potential
  - Discrete solvent effects
  - Division of system:



  - EFP is much less computationally expensive!!

EFP Method

- Effect of “solvent” molecules (fragments) added as one-electron terms to *ab initio* Hamiltonian, $\mathbf{H_{AR}}$

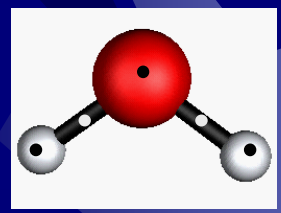
$$H_{system} = H_{AR} + V$$

- **FRAGMENT** potential (V):
  - Obtained by separate AI calculations
  - Depends on properties of isolated molecules
  - Can be systematically improved
  - Only one-electron integrals!

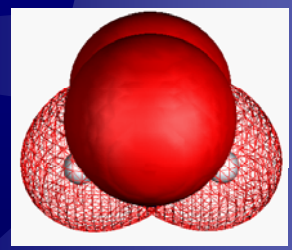
EFP Method

$$V_{el}(\mu,s) = \sum_{k=1}^{K} V_k^{Elec}(\mu,s) + \sum_{l=1}^{L} V_l^{Pol}(\mu,s) + \sum_{m=1}^{M} V_m^{\mathrm{Re}\,p}(\mu,s)$$

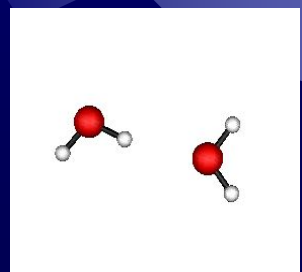
- **Electrostatics**: Coulomb interactions
  - Distributed multipolar expansion up to octupoles



- **Polarization**: Dipole/induced dipole potential
  - Localized molecular orbital (LMO) polarizability expansion
  - Induced dipoles iterated to self-consistency



- **Exchange repulsion/charge transfer**: Remainder term
  - EFP1: fit to functional form

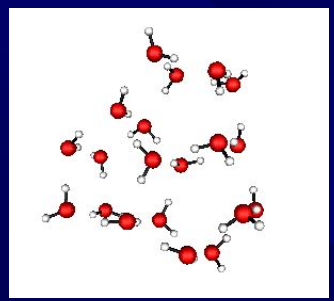


Further Developments

- EFP1/DFT:
  - Initial *ab initio* calculations based on DFT (versus EFP1/HF)
- EFP1/MP2:
  - Initial calculations based on MP2
  - Dispersion term from MP2 included
- EFP2: Generalize the EFP method
  - Exchange repulsion from first principles (NO FITS!)
  - Generalized dispersion term in progress

EFP Method in Use

- EFP1/HF has been shown to represent water clusters and solvation reactions well
  - Reproduce *ab initio* results
- First test of EFP to reproduce bulk behavior:
  - Implementation of EFP and Molecular Dynamics (MD) within GAMESS



Molecular Dynamics + EFP

- Solve Newton's equations of motion to propagate a system through time
  - Use EFP to generate energy and gradients (forces)

•Do i = 1, number of simulation steps

➢Calculate PE and gradients ➔ forces for particle at time t

➢Solve equations of motion for each particle to obtain KE at time t and new positions at time t + dt

•End do

- Currently implemented:
  - EFP1/HF, EFP1/DFT, EFP1/MP2*
  - SPC/E
  - EFP2/HF* and AI MD*

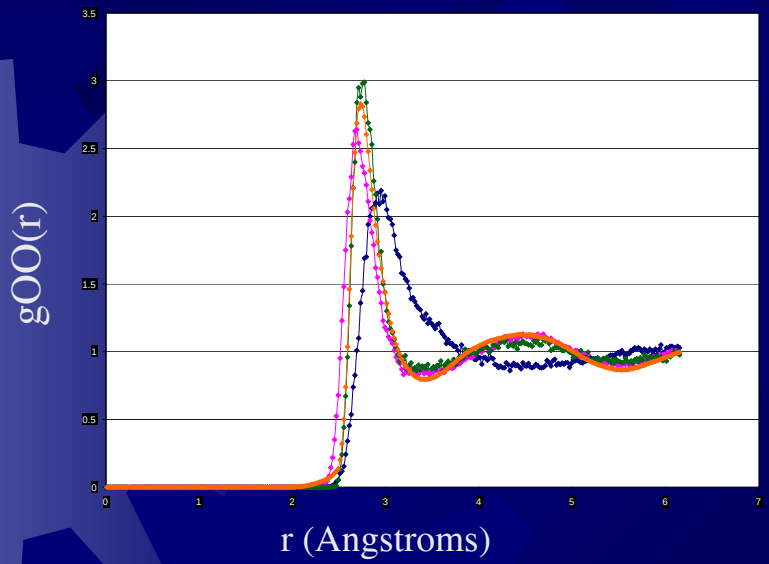
MD + EFP

- Integration:
  - EFP water is a rigid molecule--center of mass motion
    - Translational motion: leapfrog algorithm
    - Rotational motion: quaternions and modified leapfrog
- Ensembles:
  - NVE (constant energy)
  - NVT (constant temperature)
    - Based on velocity scaling: rescale by $\sqrt{\frac{T_0}{T(t)}}$
- Periodic boundary conditions and minimum image convention implemented for EFP-EFP MD

MD + EFP

- Objectives:
  - Compare EFP with other water potentials and experimental results for bulk water
- Radial distribution function (RDF)
  - Gives information on how molecules pack in neighbor ‘shells’, as well as average structure
  - Can be measured spectroscopically (X-ray or neutron diffraction)
  - 3 site-site RDFs for water (gOO(r), gOH(r), gHH(r))

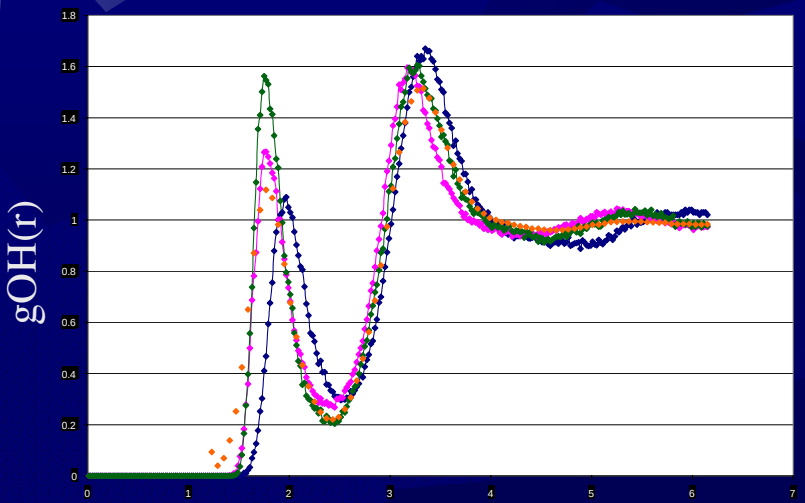
RDF--62 waters

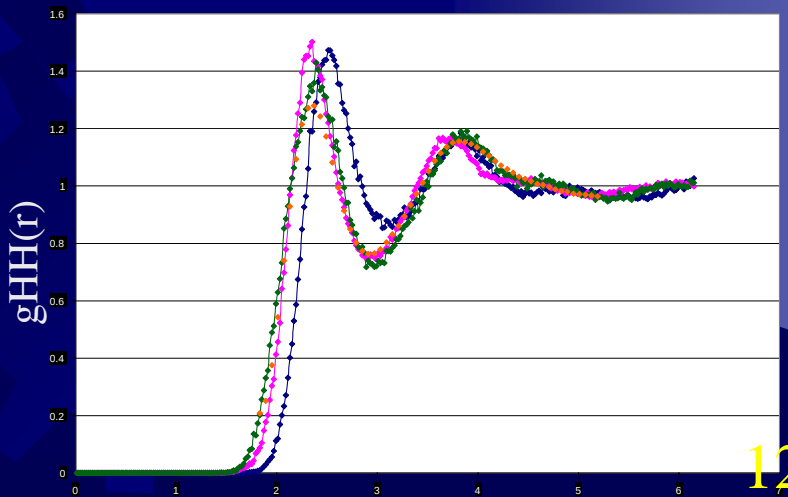


Initial structure: 62 waters,
26 ps equilibration

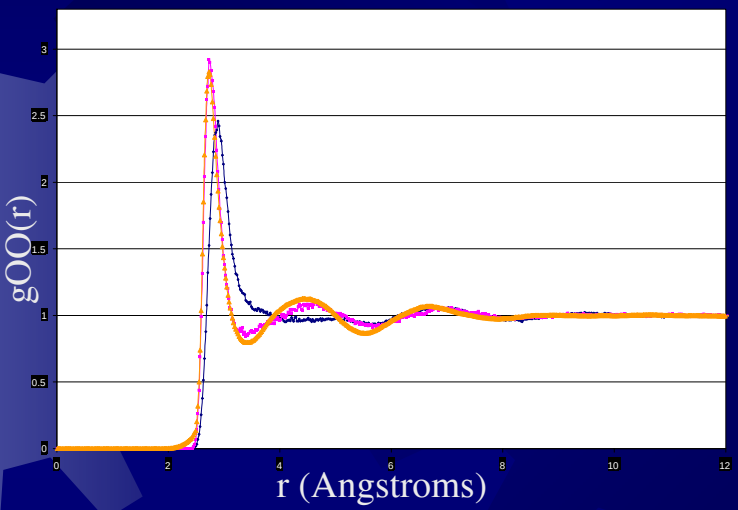
Timestep size = 1 fs,
Simulation = 5000 fs

EFP1/HF--NVT
EFP1/DFT--NVT
SPC/E--NVT
Experimental*





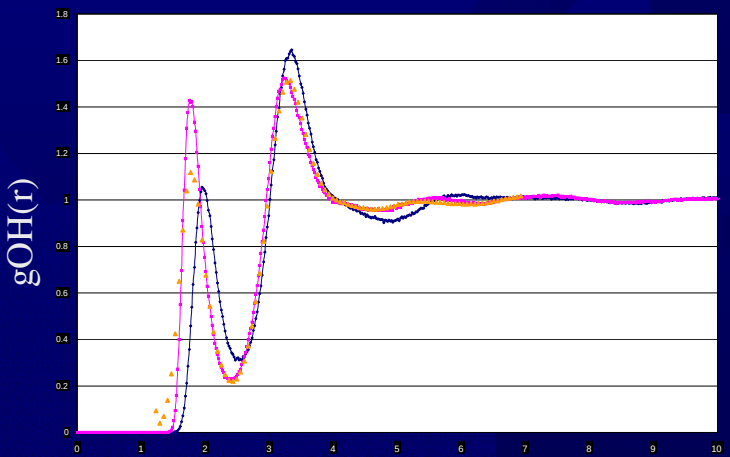
RDF--512 waters

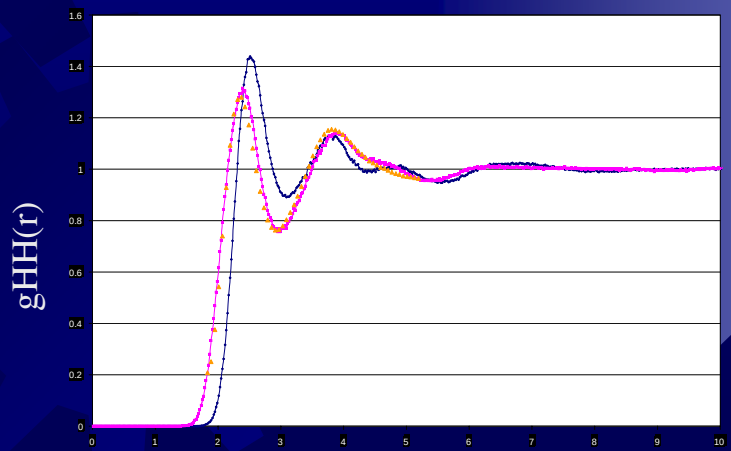


Initial structure: 512 waters, 7.5 ps equilibration

Timestep size = 1 fs, Simulation = 5000 fs

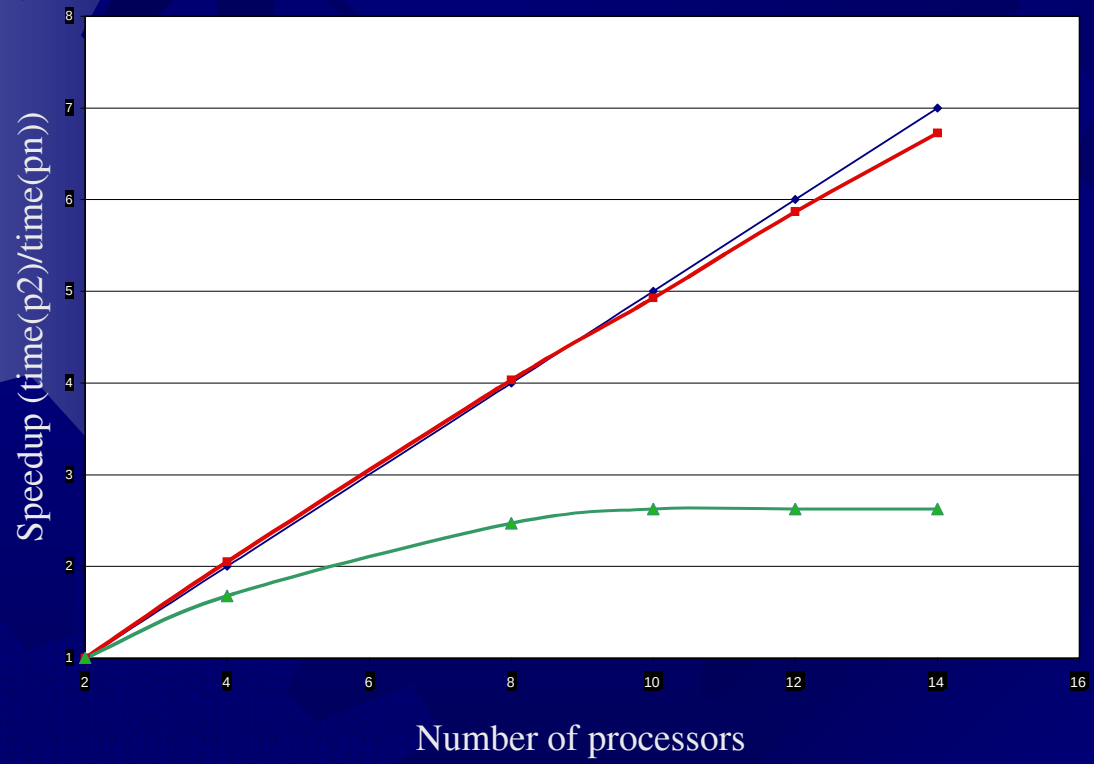
EFP1/HF--NVT
SPC/E--NVT
Experimental*





Exp (gOO): X-ray; Sorenson et. al. J. Chem. Phys. **113**,9149(2000).; Exp (gOH, gHH): Neutron Diffraction; Soper et. al.

Parallel EFP:
Speedup curves (energy + gradient)



"Raw" times:

512 EFP1/HF waters:

Serial (p=1)=352.2 sec

Parallel(p=14)=39.8 sec

Conclusions/Future Plans

- EFP is a viable method for solvation
- Continuation of EFP and MD development
  - Extensions such as treatment of long range forces, use of simplectic methods (versus quaternions), inclusion of more ensemble options
  - Treatment of AI-EFP MD
- Utilization of parallel EFP with MD

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